SUPPLEMENTAL MATERIAL

The Greening of Pesticide-Environment Interactions: Some Personal Observations

John E. Casida

Table of Contents

Supplemental Figure 1. Pesticide-environment interactions.

Supplemental Figure 2. DDT discoverer Paul Müller and anti-DDT wildlife scientist and *Silent Spring* author Rachel Carson. Photo of Müller by the author in 1958. Photo of Rachel Carson about 1944.

Supplemental Figure 3. Insecticides from chlorination of benzene and camphene consist of polychlorocycloalkane isomer mixtures with the most active isomer as a minor component.

Supplemental Figure 4. 2,4,5-T herbicide is banned due to an "exquisitely toxic" tetrachlorodibenzodioxin (TCDD) impurity.

Supplemental Figure 5. DDT metabolism yields a persistent environmental pollutant (DDE), a miticide (dicofol), a plant growth regulator (DDA) and another insecticide (DDD).

Supplemental Figure 6. Metabolic oxidative activation of phosphorothiolate insecticides profenofos (A) and acephate (B).

Supplemental Figure 7. Photostabilization of a pyrethroid (A) and a neonicotinoid (B) by replacing photolabile substituents.

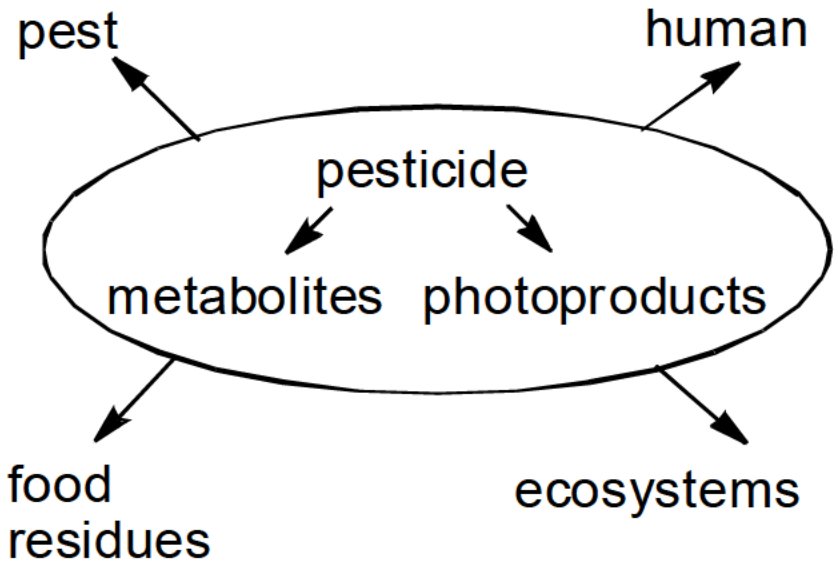
Supplemental Figure 8. Photoactivation of oxime ether pyrethroid.

Supplemental Figure 9. Botanical insecticides in umbelliferae foods (A) and along with a toxic contaminant in Chinese medicinal plants (B)

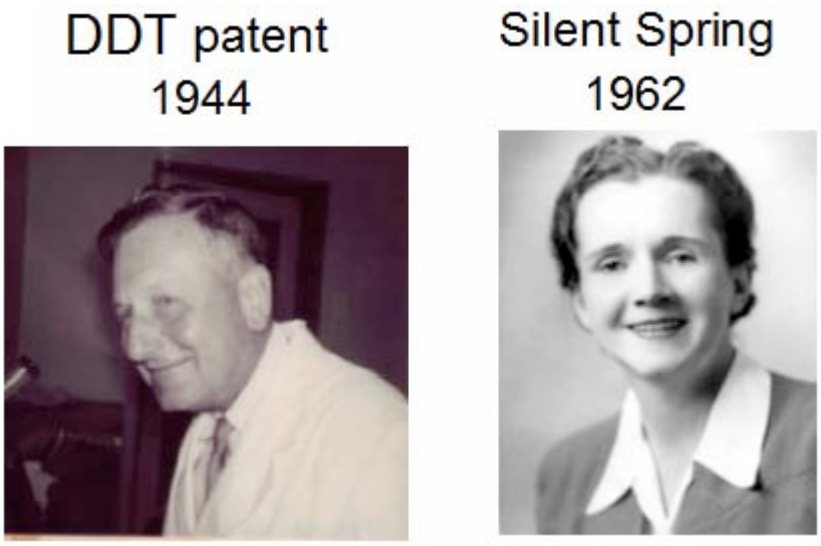
Supplemental Figure 10. Secondary targets of organophosphorus insecticides.

Supplemental Figure 11. Causal agents in three cases of massive fish kills by accident [endosulfan (A) and metam sodium (B)] and intent (derris containing rotenone) (C).

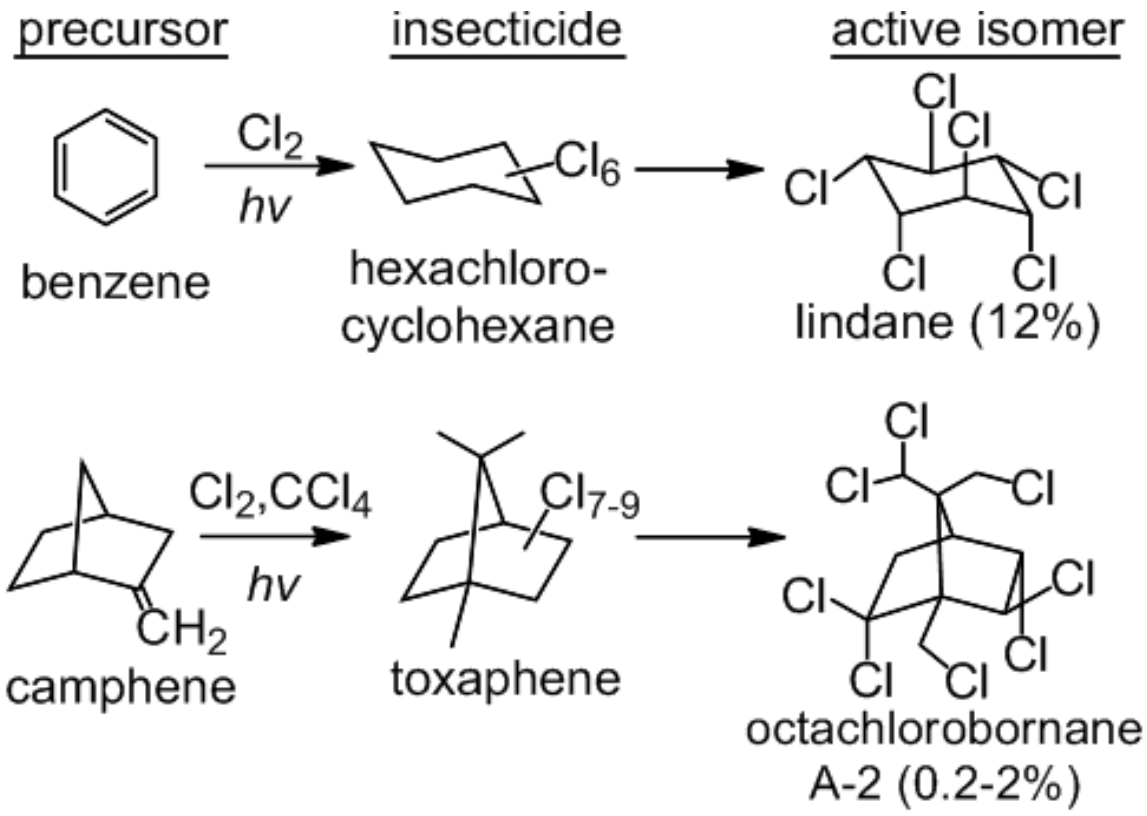
Supplemental Figure 12. Fenvalerate and two non-ester analogs of reduced fish toxicity



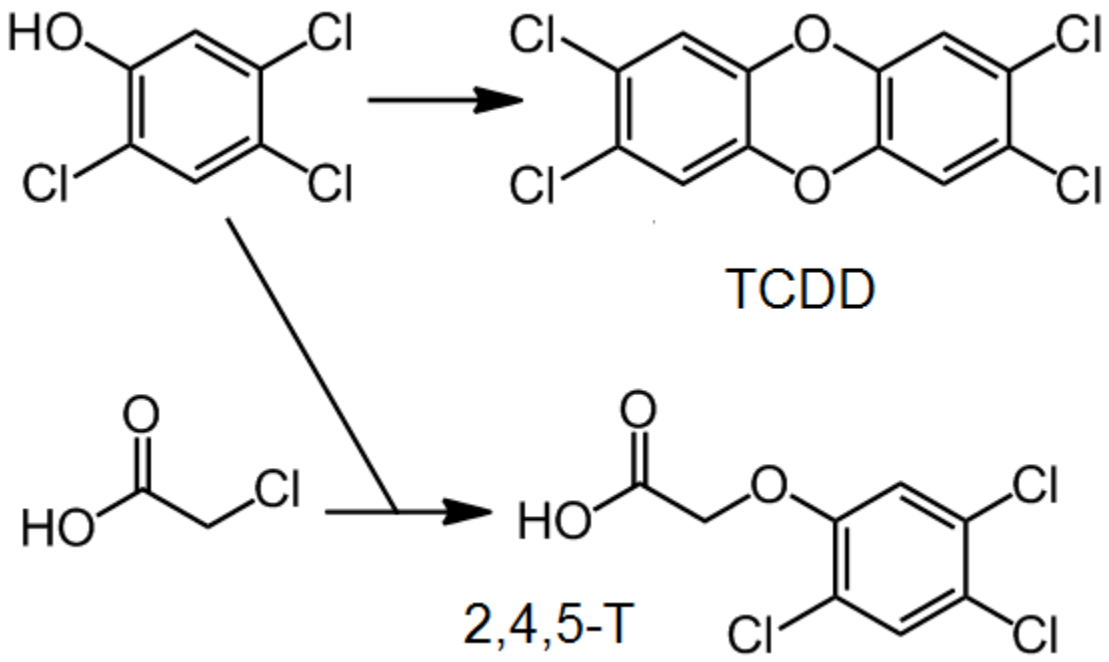
Supplemental Material, Figure 1. Pesticide-environment interactions.



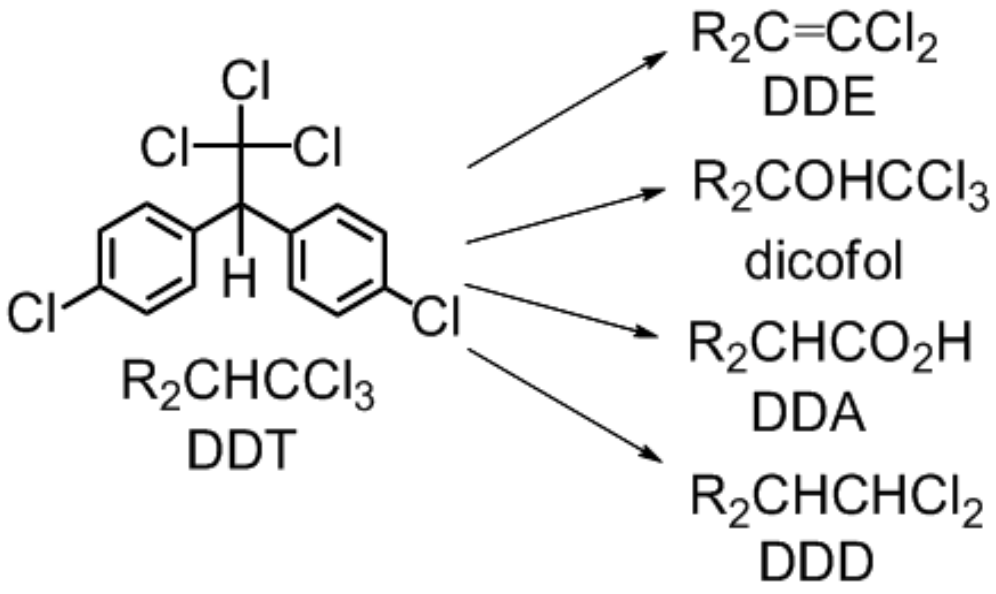
Supplemental Material, Figure 2. DDT discoverer Paul Müller and anti-DDT wildlife scientist and *Silent Spring* author Rachel Carson. Photo of Müller by the author in 1958. Photo of Rachel Carson about 1944.



Supplemental Material, Figure 3. Insecticides from chlorination of benzene and camphene consist of polychlorocycloalkane isomer mixtures with the most active isomer as a minor component.



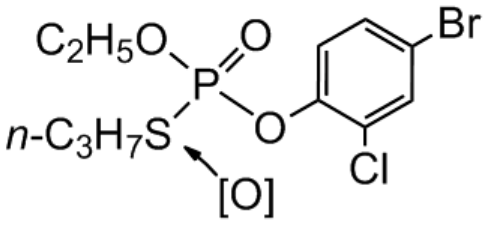
Supplemental Material, Figure 4. 2,4,5-T herbicide is banned due to an "exquisitely toxic" tetrachlorodibenzodioxin (TCDD) impurity.



Supplemental Material, Figure 5. DDT metabolism yields a persistent environmental pollutant (DDE), a miticide (dicofol), a plant growth regulator (DDA) and another insecticide (DDD).

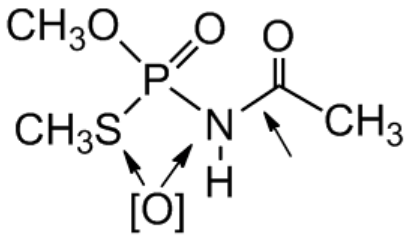
A. PROFENOFOS

sulfoxidation
activates (-)
and detoxifies (+)



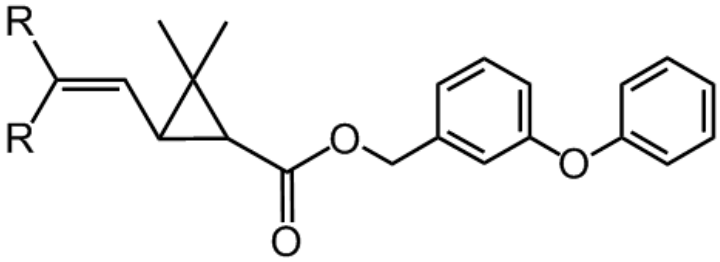
B. ACEPHATE AND METHAMIDOPHOS

activated by
amidase deacetyl-
ation and possibly
S- or *N*- oxidation



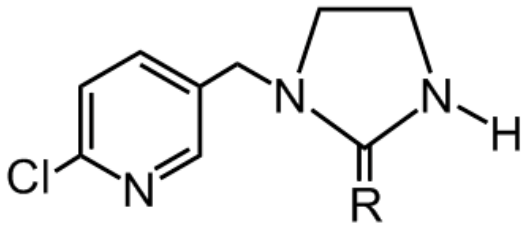
Supplemental Material, Figure 6. Metabolic oxidative activation of phosphorothiolate insecticides profenofos (A) and acephate (B).

A. PYRETHROIDS



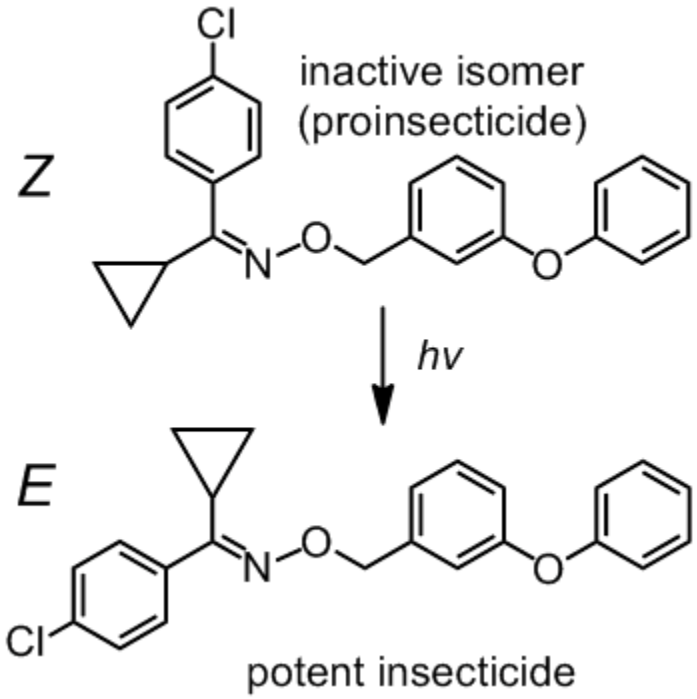
phenothrin (R = CH_3) ⟶ permethrin (R = Cl)

B. NEONICOTINOIDS



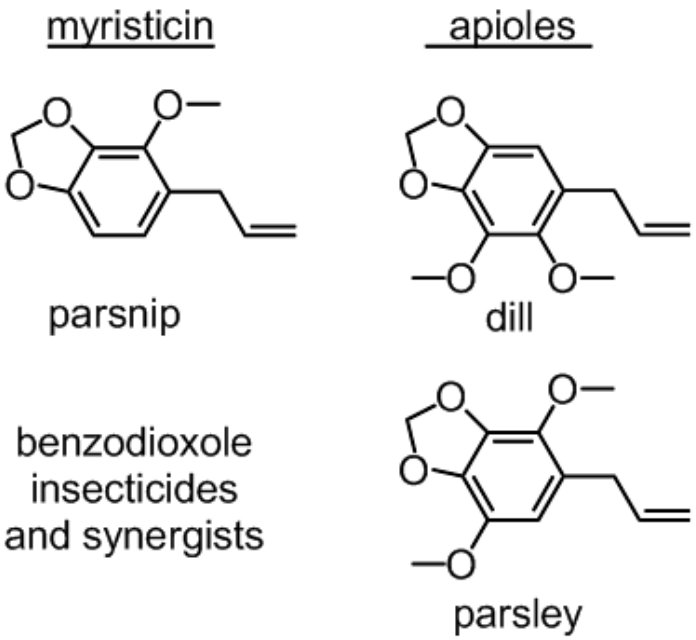
prototype (R = $CHNO_2$) imidacloprid (R = N-NO_2)

Supplemental Material, Figure 7. Photostabilization of a pyrethroid (A) and a neonicotinoid (B) by replacing photolabile substituents.

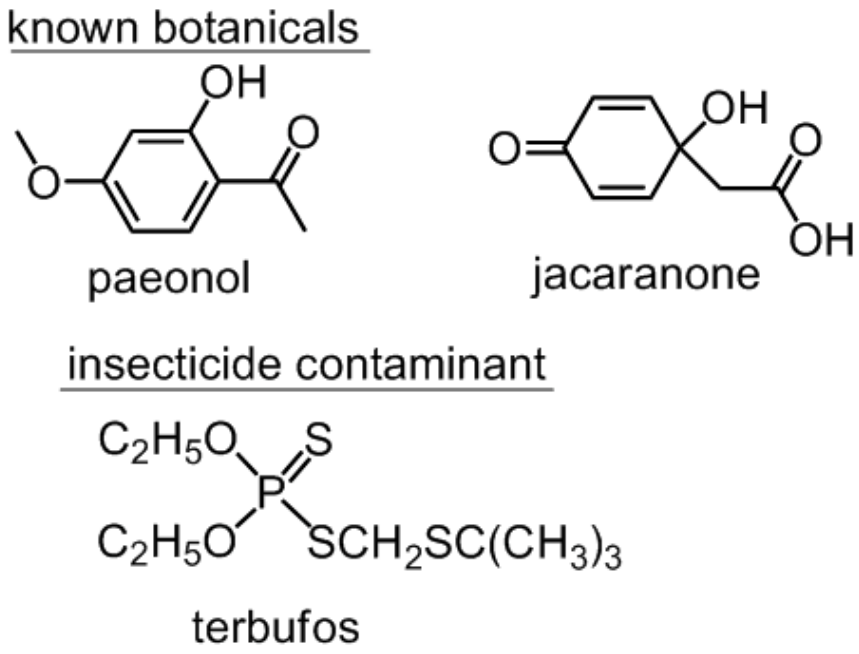


Supplemental Material, Figure 8. Photoactivation of oxime ether pyrethroid.

A. UMBELLIFERAE FOODS



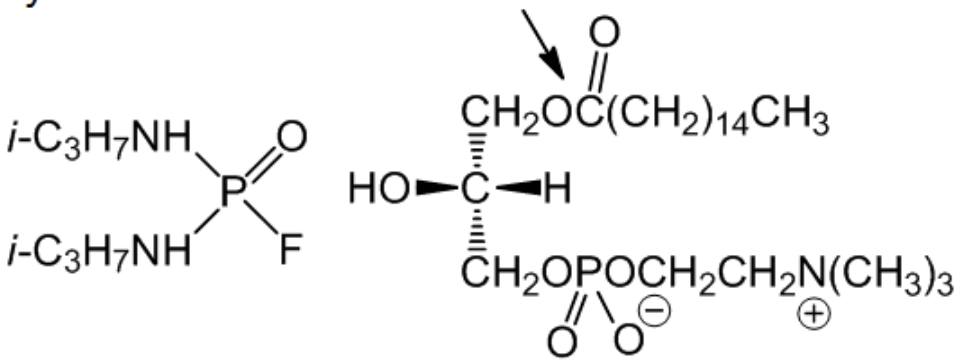
B. MEDICINAL PLANTS



Supplemental Material, Figure 9. Botanical insecticides in umbelliferae foods (A) and along with a toxic contaminant in Chinese medicinal plants (B)

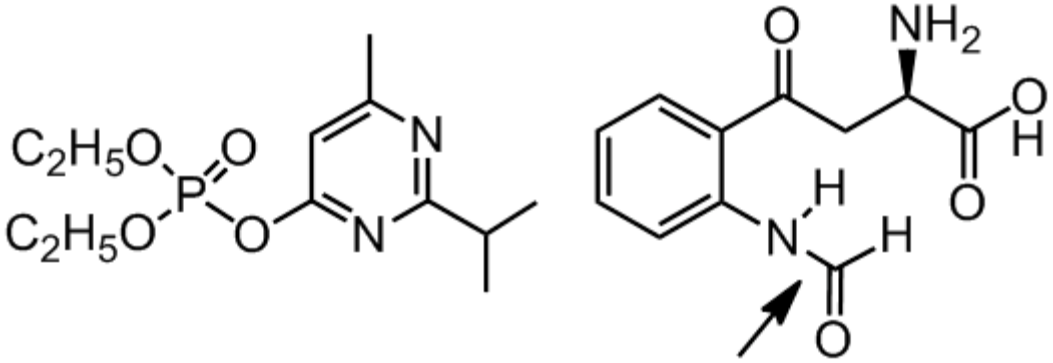
A. DELAYED NEUROPATHY (OPIDN)

mipafox inhibits lysophosphatidylcholine hydrolase



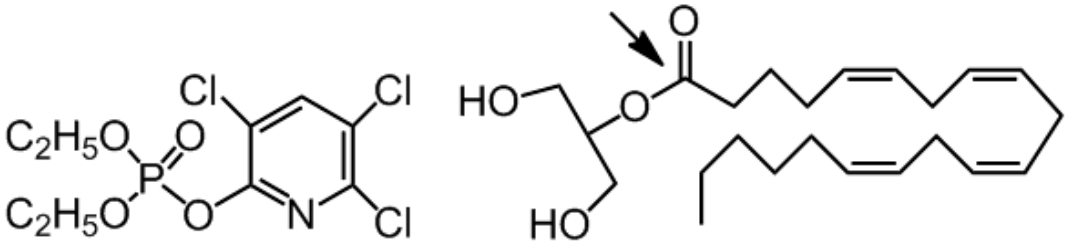
B. AVIAN TERATOGENESIS

diazoxon inhibits kynurenine formamidase



C. CANNABINOID SYNDROME

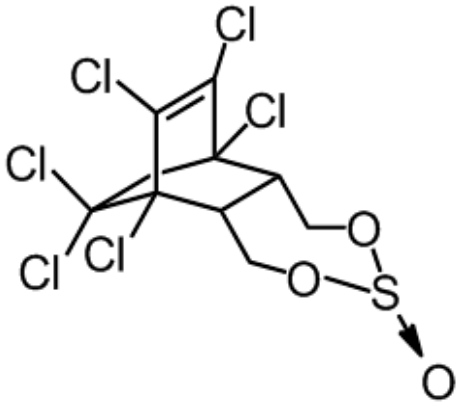
chlorpyrifos oxon inhibits monoacylglycerol lipase



Supplemental Material, Figure 10. Secondary targets of organophosphorus insecticides.

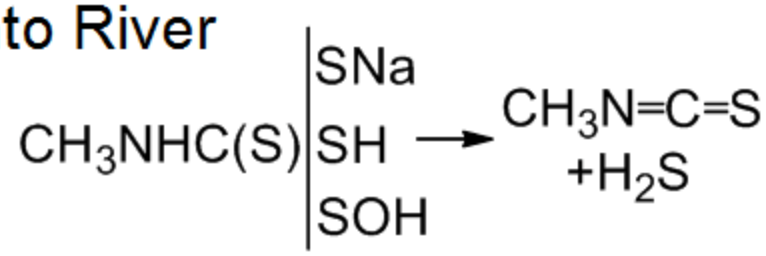
A. ENDOSULFAN

in Rhine river
gave massive
fish kill



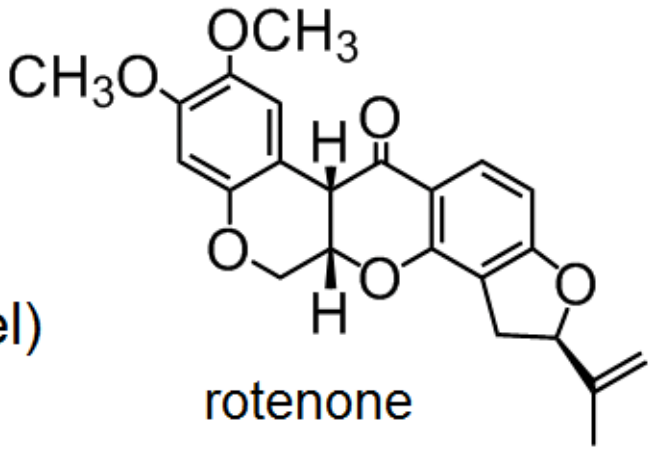
B. METAM SODIUM

in Sacramento River
gave major
ecological
changes

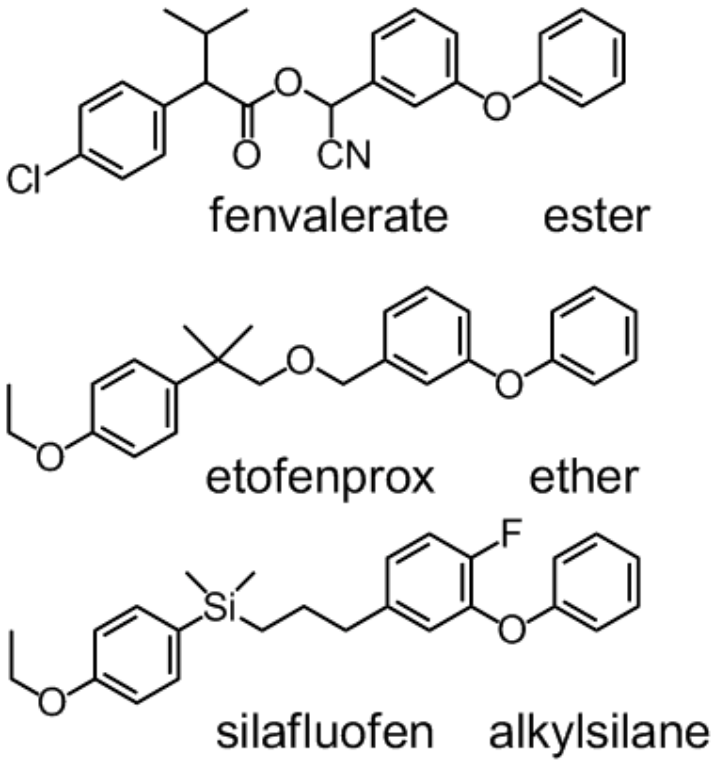


C. DERRIS PISCICIDE

in Lake Davis
as piscicide
(multicomponent
anticancer and
Parkinson's model)



Supplemental Material, Figure 11. Causal agents in three cases of massive fish kills by accident [endosulfan (A) and metam sodium (B)] and intent (derris containing rotenone) (C).



Supplemental Material, Figure 12. Fenvalerate and two non-ester analogs of reduced fish toxicity